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Note

THE DETERMINATION OF GYPSUM AND LIME IN SMALL SAMPLES OF SET PLASTER BY A DSC—COMPUTER METHOD

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This work arose from the need to analyse quantitatively very small samples (typically 1—2 mg) of set plaster for gypsum and lime. The DSC method relies on the dehydration of gypsum and dehydroxylation of lime occurring at sufficiently different temperatures for the endothermic peaks to be well resolved, although a small exothermic effect from calcium sulphate reduces the measured response of the dehydroxylation reaction. The results of a preliminary investigation into the suitability of a DSC—computer method for the analysis of set plaster are presented in this paper.

EXPERIMENTAL

Apparatus

A Dupont thermal analyser (model 990), equipped with a standard DSC cell (model 900600-902) and interfaced to a DEC PDP 11-10 (28k core) computer by means of a Hewlett Packard digital voltmeter (model HP3430D), a BCD—binary converter and a DEC DR-11C general input—output device, was used for all measurements.

A data rate of 4 Hz was used to take advantage of the digital voltmeter time constant to reduce noise, which in turn rendered digital smoothing unnecessary.

The BCD—binary converter used a cascade of 15 6 bit BCD—binary read-only memories (National Semiconductor DM 74184M) to convert the 4.5 digit BCD output of the DVM to bit binary for acceptance by the DR-11C. Computer output was displayed on a Tektronix 4010 graphics terminal and 4662 graphics plotter. A schematic diagram of the system is given in Fig. 1. Integration limits were selected visually and transmitted to the computer using the graphics input mode of the terminal.

All programs have been written in FOCAL, under the RT-11 operating system, as this was found to be the most convenient language for controlling the DR-11C, digital voltmeter, graphics terminal and plotter.

Fig. 1. Computer interfaced thermal analysis system.

Preparation of samples

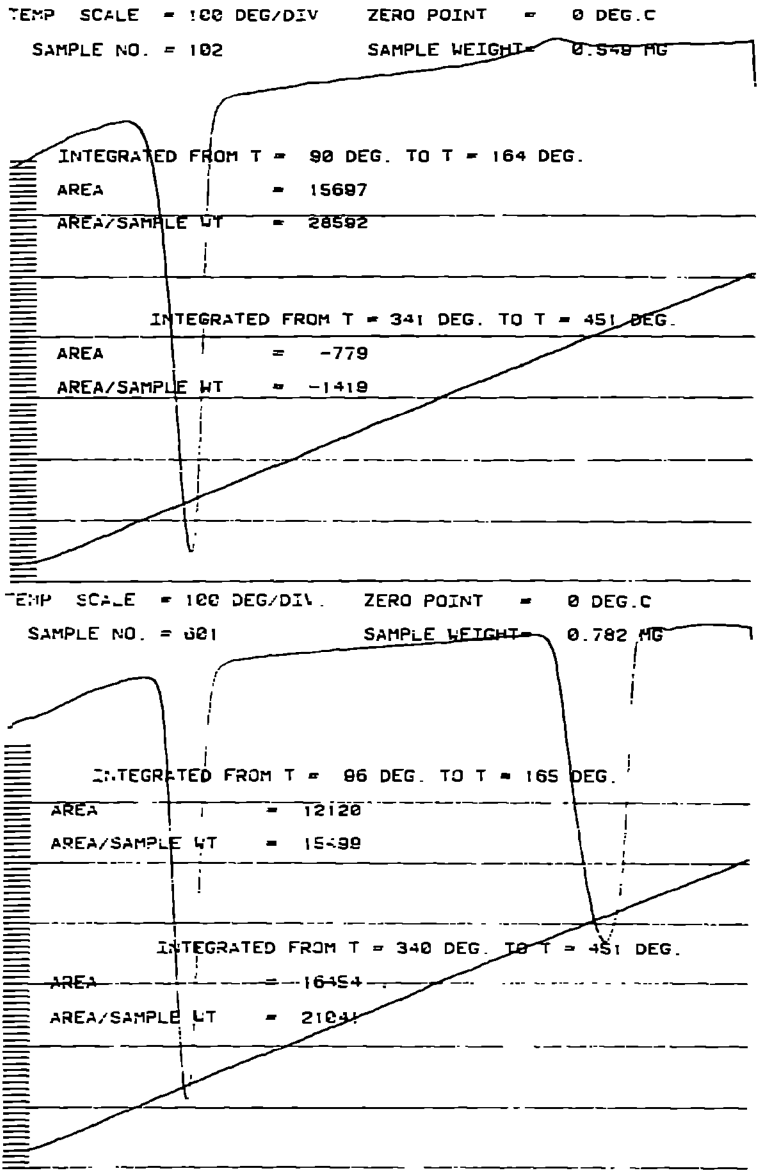
Plaster samples were prepared from a commercial plaster of paris with addition of varying amounts of A.R. calcium hydroxide. The dry mixtures were homogenized by milling in a porcelain ball mill (Erweka Apparatebau, type KU1). Set plaster samples were prepared by mixing 5 g deionized water with 10 g plaster—calcium hydroxide mixture in plastic weighing trays (75 mm × 75 mm × 25 mm). The samples were left to set for a minimum of 2 h, when they were broken up and stored in stoppered bottles. The set plaster was dried in vacuo at room temperature (25°C) and ground to —125 μ under nitrogen. Powdered samples were vacuum dried and stored under nitrogen in stoppered tubes.

The gypsum content of the samples was determined from the weight loss of 1 g vacuum dried sample heated to constant weight at 215—230°C [1]. The ASTM Available Lime Index procedure was used to determine the calcium hydroxide content [2].

TABLE 1

Gypsum and calcium hydroxide content of set plaster samples determined by ASTM methods

Sample No.	% Gypsum	% Lime
1	95.1	0
2	83.4	6.41
3	74.7	14.1
4	64.8	21.7
5	56.6	31.3
6	48.5	37.0



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TEMP SCALE   = 100 DEG/DIV      ZERO POINT   =    0 DEG.C
 SAMPLE NO. = 102               SAMPLE WEIGHT=    0.549 MG

   INTEGRATED FROM T =  90 DEG. TO T = 164 DEG.
   AREA                =  15697
   AREA/SAMPLE WT      =  28592

           INTEGRATED FROM T = 341 DEG. TO T = 451 DEG.
   AREA                =   -779
   AREA/SAMPLE WT      =  -1419

TEMP SCALE   = 100 DEG/DIV.     ZERO POINT   =    0 DEG.C
 SAMPLE NO. = 601               SAMPLE WEIGHT=    0.782 MG

   INTEGRATED FROM T =  86 DEG. TO T = 165 DEG.
   AREA                =  12120
   AREA/SAMPLE WT      =  15499

           INTEGRATED FROM T = 340 DEG. TO T = 451 DEG.
   AREA                =  16454
   AREA/SAMPLE WT      =  21041
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Fig. 2. Computer printouts for samples 1 and 6.

Procedure

Catchweight samples (0.55—2.02 mg) were weighed into aluminium pans on a microbalance. The samples were consolidated in the pans by gentle tamping with a polished steel rod and placed in the DSC cell without closing the pans. The samples were heated from ambient to 500° C at a heating rate of 50° C min^{-1} with a flowing nitrogen atmosphere of 100 ml min^{-1}.

RESULTS AND DISCUSSION

The gypsum and lime content of the set plasters, as determined by the standard ASTM methods, are presented in Table 1, and a typical output from the DSC-computer system is shown in Fig. 2. Two heating rates of 20°C $\min^{-1}$ and 50°C $\min^{-1}$ were examined, the latter being chosen because it gave improved peak definition and a shorter analysis time. Each sample could be analysed within 15—20 min.

The results obtained for gypsum (33 points, coefficient of variation 3.65%) and lime (25 points, coefficient of variation 5.9%) are shown in Figs. 3 and 4, respectively. The lime results are uncorrected for the exothermic effect from calcium sulphate.

From a gypsum sample containing no lime, the area of the exotherm occurring between 350 and 400°C was measured, and the ratio of this peak to the gypsum dehydration peak calculated to be 0.051 ± 0.005 (coefficient of variation 11.4%). This factor was used to correct the lime dehydroxylation peak areas for the effect of the exotherm. For samples containing high gypsum and low lime contents, the correction values become of the same order as those obtained for the lime peak areas, and large error factors result. On the other hand, for high lime and low gypsum contents the correction factor becomes increasingly reduced in magnitude, and it may be simpler and more reliable to ignore the correction factor for samples in the region >10% lime and <90% gypsum.

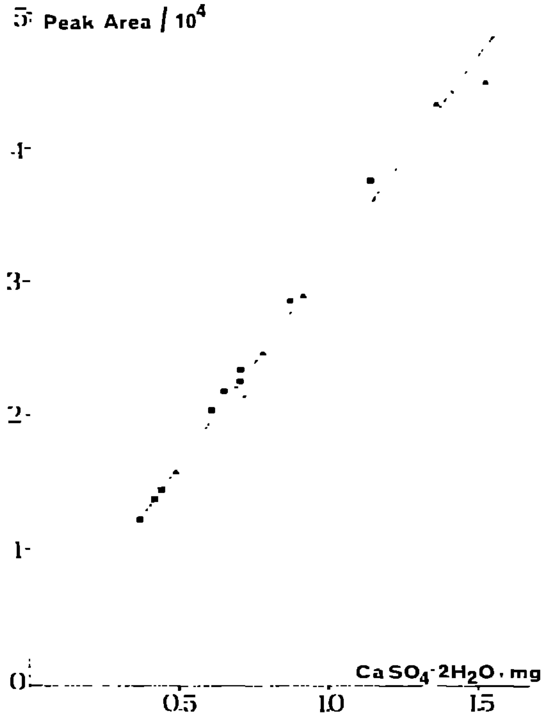

Fig. 3. Plot of area of gypsum dehydration endotherm vs. mass of $CaSO_4 \cdot 2H_2O$ in standard samples 1—6. Line of best fit is shown. □ = 1, ▽ = 2, ▲ = 3, ● = 4, ○ = 5, ■ = 6.

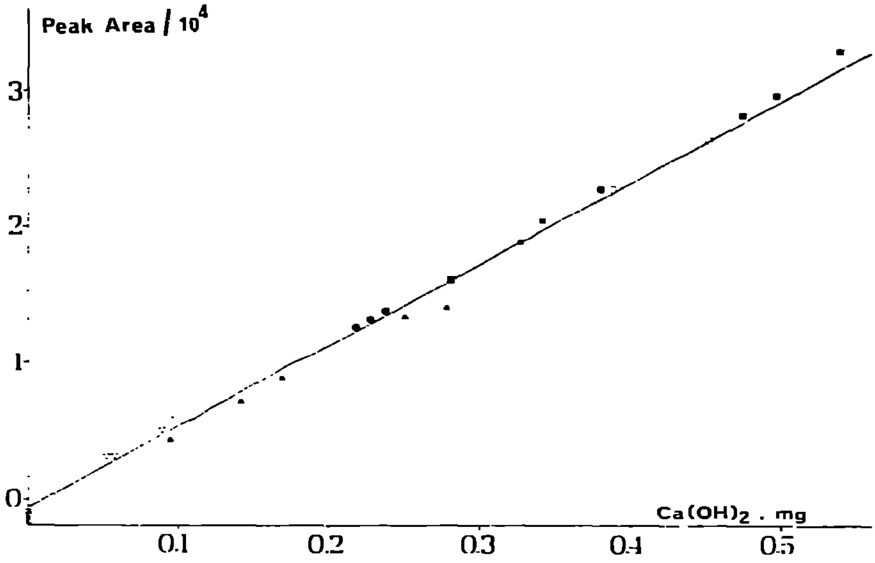

Fig. 4. Plot of area of calcium hydroxide dehydroxylation endotherm (uncorrected for $CaSO_4$ exotherm) vs. mass of $Ca(OH)_2$ in standard samples 1—6. Line of best fit is shown. □ = 1, ▽ = 2, ▲ = 3, ● = 4, ○ = 5, ■ = 6.

The results for both gypsum and lime indicate that the DSC—computer technique can provide a rapid and accurate method of analysis of very small samples of set plaster. Figures 3 and 4 were used as calibration curves for the estimation of gypsum and lime in samples (0.5—1 mg) of wall plaster. These samples were obtained with minimal damage to the surface of the walls, and were too small for analysis by conventional methods.

REFERENCES

1 ASTM Standard C471-75, Annual Book of ASTM Standards, 1976, Part 13, p. 302.
2 ASTM Standard C25-72, Annual Book of ASTM Standards, 1976, Part 13, p. 23.